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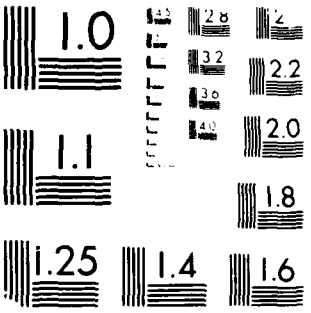

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Progress is described on study of a new class of potential excimer lasers based on diffuse bands of the alkali metal vapors. In particular, the violet diffuse bands of sodium vapor and the yellow diffuse bands of potassium vapor have been shown by detailed modeling of single vibrational-rotational level emission to be each composed of overlapping singlet and triplet "excimer" emission continua of the diatomic molecule. The gain and low absorption loss previously found in the violet and yellow with laser optical pumping of sodium vapor and potassium vapor, respectively, have been quantitatively examined. Prospects for laser oscillation appear to be good at low pressures where quenching is not dominant. Free-bound-free spectra (which include only the triplet portion of the diffuse bands) have been produced and analyzed in sodium, potassium, rubidium and cesium.

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Final Technical Report

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Air Force Office of Scientific Research grant

AFOSR-84-0178, "Alkali Metal Diffuse Band Lasers"

for

June 1, 1986-May 31, 1987

William C. Stwalley, Principal Investigator
Professor of Chemistry and Physics and
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1. Abstract

Progress is described on study of a new class of potential excimer lasers based on diffuse bands of the alkali metal vapors. In particular, the violet diffuse bands of sodium vapor and the yellow diffuse bands of potassium vapor have been shown by detailed modeling of single vibrational-rotational level emission to be each composed of overlapping singlet and triplet "excimer" emission continua of the diatomic molecule. The gain and low absorption loss previously found in the violet and yellow with laser optical pumping of sodium vapor and potassium vapor, respectively, have been quantitatively examined. Prospects for laser oscillation appear to be good at low pressures where quenching is not dominant. Free-bound-free spectra (which include only the triplet portion of the diffuse bands) have been produced and analyzed in sodium, potassium, rubidium and cesium.

2. Research Objectives

The objectives of this project are as follows:

a. To observe diffuse band emission spectra in alkali metal vapors.

b. To analyze these spectra in terms of the relevant potential energy curves and transition moments.

c. To construct new excimer (bound-free) lasers based on these spectra.

d. To assist Physical Sciences, Inc. (Andover, Massachusetts) in their attempted demonstration of a near infrared solar-pumped sodium vapor laser.

The progress in each of these areas is described below in Sections 3. a., b., c. and d., respectively.

3. Research Progress

a. Observation of diffuse band emission spectra in alkali metal vapors

Partly because of the optics and ionization problems in strong UV pumping of sodium vapor, we have spent more time on the visible-laser-pumped heavier alkali metals (especially potassium) than originally anticipated.

In particular, the triplet portions of the alkali vapor diffuse bands (in Na, K, Rb and Cs) have been directly excited for the first time (free → bound absorption followed by bound → free emission). A letter (4. 1.) and full paper (4. b.) describing this new technique for isolating the triplet emission have been submitted; the Ph.D. thesis of W. T. Luh presents most of the basic experimental results. Some new previously unobserved lithium diffuse bands in the violet have been found (papers 4. d., e.) using a variety of different excitation wavelengths.

b. Analysis of diffuse band spectra

The major items of progress in this area were the unequivocal establishment of the correct electronic assignments of the violet bands of sodium vapor (publications 4. a. and f.) and the yellow bands of potassium vapor (publications 4 b., c.). In particular, by exciting single vibrational-rotational levels of the $2^1\Sigma_u^+$ state and the $2^3\Pi_g$ state of Na_2 and K_2 we have established that the violet bands of sodium vapor and the yellow bands of potassium vapor are in fact overlapping singlet and triplet bands. The detailed assignments for Na_2 are $2^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ (peaking near 452 nm) and $2^3\Pi_g \rightarrow 1^3\Sigma_u^+$ (peaking near 436 nm). Thus the variability of the ratio between the 436 nm and 452 nm emission peaks (for both of which we have previously shown there is significant gain) is now understood for the first time. The assignments in potassium include overlapping singlet and triplet emissions ($2^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$, peaking near 570 nm; $2^3\Pi_g \rightarrow 1^3\Sigma_u^+$, peaking near 575 nm).

Detailed modeling of free-bound-free spectra has been carried out for the first time for the potassium $2^3\Pi_g$ - $1^3\Sigma_u^+$ case. Preliminary results (see publication 4. j.) report encouraging but not perfect agreement.

c. Construction of new excimer (bound-free) lasers based on diffuse band spectra.

A "recirculating supersonic molecular beam oven" (RSMBO), was used to provide direct optical access to a thin "sheet" of sodium or potassium vapor for attemped laser oscillation. This oven is now being modified (improved insulation and heating) to allow for high pressure (> 1 torr) operation. The heat pipe trough (developed at Physical Sciences; see d. and paper 4. g.) may also be used in the future. Also we will have available beginning in August a 4.5 kW 10 cm long mercury lamp and power supply (primary use: pump-ing a 60 watt cw alexandrite laser, the second of its kind, custom built by Allied Corporation). We plan to attempt lamp optical pumping with this equipment once laser optical pumping is successful.

An additional interesting possibility is chemical pumping; J. L. Gole (Georgia Tech) has seen strong violet and near ultraviolet chemiluminescence in sodium-halogen reactions which appears to correlate well with our calculations of Na_2 $2^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ "violet band" emission (the ultraviolet features are bound-bound transitions). We have sent him copies of our detailed radiative transition probabilities, which he finds give reasonable agreement with his spectra, assuming vibrationally hot Na_2 $2^1\Sigma_u^+$ molecules.

d. Assistance to Physical Sciences, Inc. (Andover, Massachusetts) in their attempted demonstration of a near infrared solar-pumped sodium vapor laser

We have consulted extensively with Physical Sciences, Inc. concerning their solar-pumped near infrared sodium vapor concept, both by phone and visits. We have assisted in the modified design of their heat pipe trough, in their consideration of the kinetics of the active medium, in their laser

fluorescence temperature measurements and by providing values for the absolute bound-bound and bound-free radiative transition probabilities for all vibrational levels in the $B^1\Pi_u$ - $X^1\Sigma_g^+$ bands of Na_2 (these bands are critical to the production of a high concentration of Na*, which is in turn critical to their laser concept).

4. List of Written Publications

a. "Electronic Assignments of the Violet Bands of Sodium", G. Pichler, J. T. Bahns, K. M. Sando, W. C. Stwalley, D. D. Konowalow, L. Li and R. W. Field, Chem. Phys. Letters 129, 425 (1986).

b. "Direct Excitation Studies of the Diffuse Bands of Alkali Metal Dimers", W. T. Luh, J. T. Bahns, A. M. Lyyra, K. M. Sando, P. D. Kleiber and W. C. Stwalley, submitted to J. Chem. Phys.

c. "Electronic Assignments of the Yellow Bands of Potassium", W. T. Luh, K. M. Sando, K. P. Chakravorty, W. C. Stwalley, G. Pichler and D. D. Konowalow, Chem. Phys. Letters 131, 335 (1986).

d. "The 458 nm Diffuse Band of the Lithium Dimer", J. T. Bahns, W. C. Stwalley and G. Pichler, J. Chem. Phys., in press.

e. "Study of the Shape of the Lithium Diffuse Band by Single and Double Photon Excitation", G. Pichler, J. T. Bahns and W. C. Stwalley in Spectral Line Shapes, Volume 3, edited by F. Rostas (De Gruyter and Co., Berlin, 1985), p. 659.

f. "Electronic Assignments of the Violet Bands of Sodium", G. Pichler, J. T. Bahns, K. M. Sando, W. C. Stwalley, W. Müller, D. D. Konowalow, L. Li and R. W. Field, in Advances in Laser Science I, edited by W. C. Stwalley and M. Lapp (American Institute of Physics, New York, 1986), p. 160.

g. "New Heat Pipe Oven Devices for Broad Band Excitation Laser Studies", M. A. DeFaccio, S. J. Davis, D. I. Rosen, W. C. Stwalley and D. O. Ham, in Advances in Laser Science I, edited by W. C. Stwalley and M. Lapp (American Institute of Physics, New York, 1986), p. 165.

h. "Long Range Potential of the $A^1\Sigma_u^+$ State of Na_2 using Modulated Gain Spectroscopy", G. Chawla, H. S. Schweda, H. J. Vedder, R. W. Field, S. Churassy, A. M. Lyyra, W. T. Luh and W. C. Stwalley in Advances

in Laser Science I, edited by W. C. Stwalley and M. Lapp (American Institute of Physics, New York, 1986), p. 466.

i. "Spectroscopy of Alkali Metal Vapors under Conditions of Interest for Solar Plasma Propulsion", W. C. Stwalley, to appear in Proceedings of the January 1986 University of Dayton/AFOSR Workshop on Solar Plasma Propulsion.

j. "Free-Bound-Free Resonance Fluorescence in the K_2 Yellow Diffuse Band: Theory and Experiment", W. T. Luh, K. M. Sando, A. M. Lyyra and W. C. Stwalley, submitted to Chem. Phys. Letters.

k. "Reinvestigation of the K_2 B-X Fluorescence Excited by a Krypton Ion Laser", W. T. Luh, J. T. Bahns and W. C. Stwalley, J. Mol. Spectrosc., in press.

l. "Studies of the Diffuse Bands of K_2, Rb_2 and Cs_2", W. T. Luh, J. T. Bahns, A. M. Lyyra, K. M. Sando, P. D. Kleiber and W. C. Stwalley, in Advances in Laser Science II, edited by M. Lapp, W. C. Stwalley, and G. Kenney-Wallace (American Institute of Physics, New York, 1987), in press.

5. Professional Personnel* (University of Iowa)

a. William C. Stwalley, Principal Investigator

b. Paul D. Kleiber, Assistant Research Scientist/Assistant Professor of Physics

c. Shawn P. Heneghan, Postdoctoral Research Associate

d. Kuo-Kwang Wang, Postdoctoral Research Associate

e. A. Marjatta Lyyra, Postdoctoral Research Associate/Assistant Research Scientist

f. Wei-Tzou Luh, Graduate Student in Physical Chemistry (received Ph.D. in August 1985; passed final exam on thesis entitled "Laser Spectroscopic Studies of Alkali Metal Dimers"[+] on July 5, 1985).

g. Steve Evans, Graduate Student in Physical Chemistry

h. Juan Figueroa, Graduate Student in Chemical Physics

i. Young-June Cho, Graduate Student in Physical Chemistry (received M.S. without thesis in August 1986)

j. Vassillis Zafiropulos, Graduate Student in Physical Chemistry

k. Warren T. Zemke, Visiting Professor (Summer only)

* Other University of Iowa researchers collaborating on this research include Dr. John T. Bahns (Iowa High Technology Council support), Dr. Krishna P. Chakravorty (Visiting Research Scientist with support from the Government of India), and Professor Kenneth M. Sando (unsupported).

[+] Copy available on request.

5. Interactions - William C. Stwalley et al.

a. Papers and Seminars

i. "Diffuse and Interference Bands in Alkali Metal Dimers" Paper ME3 at the 39th Symposium on Molecular Spectroscopy (Columbus, Ohio, June 1984).

ii. "Photophysics and Photochemistry of Alkali Metal Vapors", Department of Physics, University of Missouri (St. Louis, July 1984).

iii. "Spectra and Potential Energy Curves of Alkali Metal Diatomic Molecules: Experimental Results Compared with Theory", invited paper at American Chemical Society meeting (Philadelphia, August 1984).

iv. "Photochemistry and Photophysics of Alkali Metal Vapors", Laser Seminar, University of Toronto (Toronto, October 1984).

v. "Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, Pennsylvania State University (State College, October 1984).

vi. "Photophysics and Photochemistry of Alkali Metal Vapors", invited paper, International Conference on Applications of Lasers and Electro-Optics (Boston, November 1984).

vii. "Diffuse Bands in Alkali Metal Vapors" and "Ionization and Energy Transfer in Alkali Metal Vapors", invited papers at Lasers '84 (San Francisco, December 1984).

viii. "Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, University of Michigan (Ann Arbor, January 1985).

ix. "Photophysics and Photochemistry of Alkali Metal Vapors", Combustion Research Facility, Sandia National Laboratories (Livermore, February 1985).

x. Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, University of Missouri-Rolla (August 1985).

xi. "Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, Illinois Institute of Technology (September 1985).

xii. "Electronic Assignments of the Violet Bands of Sodium", "New Heat Pipe Oven Devices for Broad Band Excitation Laser Studies", and "Long Range Potential of the $A^1\Sigma_u^+$ State of Na_2 Using Modulated Gain Spectroscopy", contributed papers, the first International Laser Science Conference (Dallas, November 1985).

[illegible] "[illegible] Alkali Metal [illegible]", [illegible] Solar Plasma [illegible] AF [illegible] Workshop [illegible] Solar Plasma [illegible] [illegible].

[illegible] "Photophysics and Photochemistry of Alkali Metal Vapors", Institute of Physics, Beijing, [illegible] University, Harbin Institute of Technology, Institute of the Salt Lake [illegible], Laser Institute [illegible], and East China Normal University ([illegible] April [illegible]).

[illegible] "Photophysics and Photochemistry of Alkali Metal Vapors", [illegible] Division, Argonne National Laboratory (May [illegible]).

[illegible] "[illegible] Pumped Alkali Metal Diffuse Band Lasers", contributed paper, Optical Society of America Annual Meeting, Seattle ([illegible]).

[illegible] "Studies of the Diffuse Bands of [illegible]", contributed paper, [illegible] International Laser [illegible] ([illegible]).

xviii "Photophysics and Photochemistry of Alkali Metal Vapors", Department of Physics, Maharishi International University ([illegible] [illegible]ber [illegible]).

xix "Photophysics and Photochemistry of Alkali Metal Vapors", Physics Division, Oak Ridge National Laboratory (November 1986).

xx "Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, University of Puerto Rico (November 1986).

xxi "Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, University of Miami (November 1986).

xxii "Photochemistry and Photophysics of Alkali Metal Vapors", Department of Chemistry, Grinnell College (January 1987).

b. Consultations

i. Visited Physical Sciences, Inc. (D. Ham, host) regarding collaboration on solar-pumped near infrared sodium vapor laser (Andover, Massachusetts, July 1984).

ii. Visited Air Force Weapons Laboratory (S. Davis, host) regarding optically pumped lasers (Albuquerque, New Mexico, October 1984).

iii. Hosted David Ham, Physical Sciences, Inc., regarding collaboration on solar-pumped near infrared sodium vapor laser (November 1984).

iv. Visited Physical Science Inc., Andover, Massachusetts (D. Ham, host) regarding collaboration on solar-pumped near infrared sodium vapor laser (Andover, Massachusetts, July and also August 1985).

v. Visited Howard Schlossberg, AFOSR regarding research progress (May 1986).

7. New Discoveries

a. Discovery of gain at ~565 nm in the yellow bands of potassium vapor.

b. Discovery that sodium and potassium visible continua represented overlapping singlet and triplet transitions ($2^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ and $2^3\Pi_g \rightarrow 1^3\Sigma_u^+$, respectively).

c. Discovery of new violet diffuse bands in lithium vapor.

d. Discovery of free-bound-free spectra in sodium, potassium, rubidium and cesium vapor which could be described and modeled in terms of $2^3\Pi_g - 1^3\Sigma_u^+$ transitions only.

To appear in Advances in Laser Science - II, edited by Marshall Lapp, William C. Stwalley and Geraldine A. Kenney-Wallace (American Institute of Physics, New York, 1987).

Studies of the Diffuse Bands of K_2, Rb_2 and Cs_2

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Abstract

Direct dye laser excitations of the K_2 yellow, Rb_2 orange and Cs_2 near infrared diffuse bands have been investigated. Experimental results are shown to be consistent with free-bound $2^3\Pi_g \leftarrow 1^3\Sigma_u^+$ excitation followed by bound-free emission between the same two states. It is found that for Rb_2 and Cs_2, spin-orbit interactions become so significant that the $2^3\Pi_g$ state is split into three component states. For Rb_2, all three spin orbit components of the $2^3\Pi_g$ state are produced in direct excitation, whereas for Cs_2, most excitation wavelengths produce only one of the three spin-orbit components.

Introduction

Diffuse bands, especially of the alkali dimers, are interesting and important since they are thought to be primarily excimer-like triplet-triplet electronic transitions in which the lower triplet state is essentially repulsive. Because of inherent population inversions and relatively broad spectral ranges, they are potentially important continuously tunable laser sources[1]. The alkali diffuse bands have been observed from the UV to the IR in absorption spectra, electric discharge excitations, and laser excitations. Moreover, Bahns and Stwalley[2] have measured significant gain in the Na_2 violet band, Dinev et al.[3] have observed the triplet-triplet IR laser emission of Na_2, and Heneghan, Chakravorty and Stwalley[4] have measured significant gain in the K_2 yellow band. Here, in order to understand the characteristics of the potential curves of the electronic states involved in the diffuse bands mentioned above, we have used direct dye laser excitations.

Experimental

Three heat-pipe ovens (K, Rb, Cs) were used in this study. The dye laser (Coherent 599-21) was pumped by an argon ion laser at

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514.5 nm. Four laser dyes, Rhodamine 560, 590 and 610, and LDS 698 (all from Exciton), were used. Their lasing spectral ranges are 540-600 nm, 570-650 nm, 601-675 nm and 688-708 nm, respectively. The former two dyes were used for K_2, the latter two for Rb_2 and Cs_2, respectively. The dye laser (usually operated multimode) was tuned at intervals of 1 nm across the wavelength ranges of the diffuse bands. For each excitation wavelength, the fluorescence spectra were taken at selected pressures (typically a few torr), resolved using a Jarrell-Ash 8200 half-meter spectrometer, detected using an RCA 4832 photomultiplier with a PAR 134 electrometer, and recorded with a Linseis LS44 strip chart recorder.

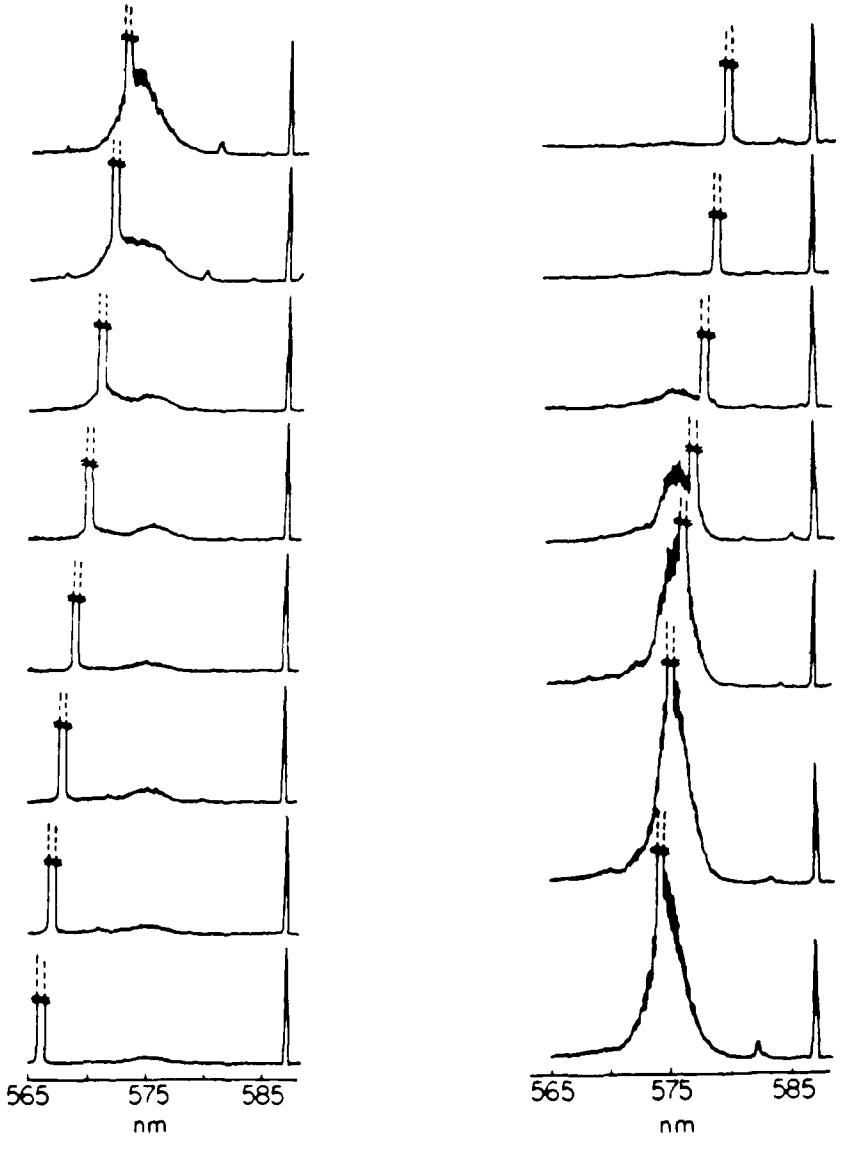
K_2 Yellow Diffuse Band

A series of fluorescence spectra is shown in Figure 1 at a pressure of 2.9 torr. The observed fluorescences are obviously unstructured continua. They can be interpreted as follows. The K_2 yellow diffuse band is presumably due to a triplet-triplet transition ($2^3\Pi_g$ - $1^3\Sigma_u^+$)[5] analogous to that observed for the Na_2 violet band[6]. If so, one may observe unstructured bound-free continuum fluorescence following nonselective free-bound excitations since, according to recent ab initio calculations[7], the lowest triplet state $1^3\Sigma_u^+$ of K_2 has a very shallow well of depth 498 cm^{-1} (which is approximately kT in this work), and one may expect most of the absorbing species in this triplet state are in free levels. Our observations in Figure 1 are indeed unstructured fluorescence continua and suggest that the $1^3\Sigma_u^+$ state is the lower electronic state involved. If the major relaxation processes of the upper electronic state bound levels are radiative, a measure of the spectrally integrated diffuse band fluorescence intensity versus excitation wavelength should resemble the absorption spectrum provided that the spectral response of the PMT detector in the range of interest is independent of wavelength. This is in fact the case if one compares our results to the reduced absorption coefficients of the same diffuse band from Johnson et al.[8] and Pichler et al.[9]. This suggests that the relaxation processes from the upper electronic state bound levels are mainly back to the lower $1^3\Sigma_u^+$ state. One expects, that bound-bound transitions are also possible, although the well depth is only about kT. To look for this, a single mode dye laser was also used through the entire diffuse band range to obtain excitation spectra. There was no clear evidence that any bound-bound triplet emission is excited. The free-free fluorescence is expected to be negligible at these wavelengths. In summary, the above observations show that one is indeed dealing with bound-free fluorescence following free-bound excitation, which energetically corresponds to the $2^3\Pi_g$ - $1^3\Sigma_u^+$ electronic transition.

Rb_2 Orange Diffuse Band

Similar diffuse band spectra were taken for Rb. One observes that these spectra are resolved into three peaks, located at 601.1 nm, 604.0 nm and 606.1 nm, respectively, unlike the single broad one

Figure 1. K_2 spectrally resolved diffuse band fluorescence in the 564-587 nm range excited by dye lasers in the range 565-578 nm at 1 nm intervals. The reference line at the right of each spectrum is Kr at 587.1 nm.



for the K_2 yellow diffuse band. It is well-known that spin-orbit interaction occurs in the multiplet electronic states with $\Lambda \neq 0$ and its significance increases rapidly with increasing numbers of electrons. Thus for the heavy molecules, the $2^3\Pi_\sigma$ state is expected to be split into three different states: $2^3\Pi_{0g}$, $2^3\Pi_{1g}$ and $2^3\Pi_{2g}$. These dye laser excitation studies show that the Rb_2 orange diffuse band

can be interpreted in terms of the $2^3\Pi_g$ - $1^3\Sigma_u^+$ transition in which the upper state is split into three component states due to spin-orbit interaction[10].

Cs_2 near infrared diffuse band

Observed fluorescence spectra for Cs_2 show diffuse band fluorescence, peaking at 718.9 nm, 712.9 nm and 707.5 nm. The separations between these three locations are larger than those of the Rb_2 orange diffuse band and are consistent with a stronger spin-orbit interaction expected for Cs_2. Because of the stronger spin-orbit interaction, the three component upper electronic states can be excited quite independently.

Summary

Dye laser direct excitation studies of the K_2 yellow, Rb_2 orange and Cs_2 near infrared diffuse bands show at least semiquantitatively that (1) they originate from an electronic transition between an upper bound triplet state and a lower repulsive triplet state; (2) from the point of view of energetics, the upper bound state is very likely the $2^3\Pi_g$ state which dissociates into a ns ground state atom and a (n-1)d excited atom; and (3) for the Rb_2 orange and Cs_2 near infrared diffuse bands, three different electronic transitions are involved because the $2^3\Pi_g$ state is split into three separate components due to the stronger spin-orbit interactions. Agreement with previous experiments is good, as summarized in Table I.

Table I. Main Peak of the $2^3\Pi_g$ - $1^3\Sigma_u^+$ Diffuse Band of Alkali Metal Dimers.

	λ_{peak}(nm)	
M_2	this work	others
Li_2	--	458.5[12]
Na_2	--	436.5[1,13]
K_2	575.0	574.5[13], 572.5[14], 575.0[10]
Rb_2	606.1	605.4[10], 606.1[15]
	604.0	603.2[10]
	601.1	600.7[10], 600.8[15]
Cs_2	718.9	718.5[10], 718[11], 718.7[16]
	712.9	712.9[10], 713[11], 712.7[16]
	707.5	705.4[10], 707[11], 706[16]

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